

Mössbauer study of novel iron(II)-dioxime complexes with branched alkyl chains

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Abstract Novel iron(II) oxime complexes with dimethyl-glyoxime, methyl-ethyl-glyoxime, methyl-isopropyl-glyoxime, $[\text{Fe}(\text{DioxH})_2\text{L}_2]$ with and without axial ligands have been synthesized. ^{57}Fe Mössbauer spectroscopy showed different spin states in complexes with short alkyl chain and with branched alkyl chain, respectively. It was shown that the asymmetry observed in the doublet line intensity of iron-bis-glyoximes is due to the texture effect. The effect of back-coordination was also studied in the case of iron-bis-dioxime complexes with branched alkyl chains, having different axial ligands.

Keywords ^{57}Fe Mössbauer spectroscopy · Novel Fe(II) oximes · Low-spin and high-spin states · Molecular geometry

1 Introduction

Oxime compounds have attracted considerable interest for the prevention and treatment of hormone-dependent cancers. The desired biological selectivity can

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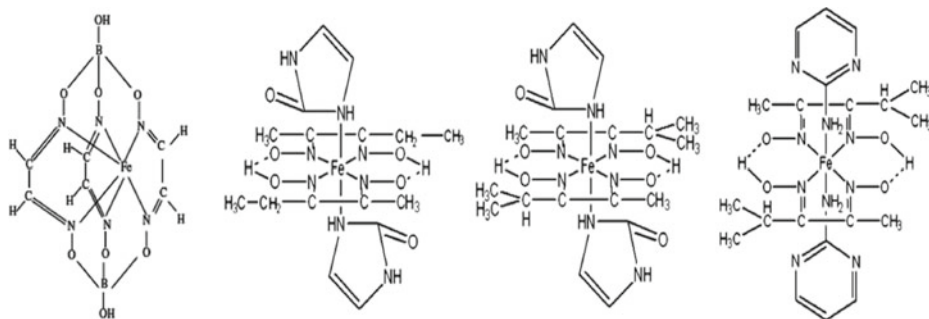


Fig. 1 The structure of $\text{Fe}(\text{glyoxime})_3(\text{BOH})_2$, $\text{Fe}(\text{Me-Et-glyoxH})_2(2\text{-imidazolidone})_2$, $\text{Fe}(\text{Me-iPr-glyoxH})_2(2\text{-imidazolidone})_2$ and $\text{Fe}(\text{Me-iPr-glyoxH})_2(2\text{-amino-pyrimidine})_2$ compounds (from left to right)

often be achieved by the special molecular geometry of oximes. Accordingly, the general focus of our study is to prepare and characterize iron oxime compounds with different spatial arrangements. In the previous researches [1–3] iron-dimethylglyoxime and iron-tris-dioximes were investigated by ^{57}Fe Mössbauer spectroscopy and DFT calculation. Iron was found in low-spin Fe^{II} state in all the investigated iron-methyl-ethyl-glyoxime complexes. It was established that iron can also occur in high-spin state in iron-bis-glyoximes when the axial ligands are absent.

The aim of the present work was to prepare novel iron oxime compounds with branched alkyl chains and to study the effect of bonds and molecular geometry on the valence and spin state of iron. For this study we applied ^{57}Fe Mössbauer spectroscopy that can give reliable information about the valence and spin state of iron.

2 Experimental

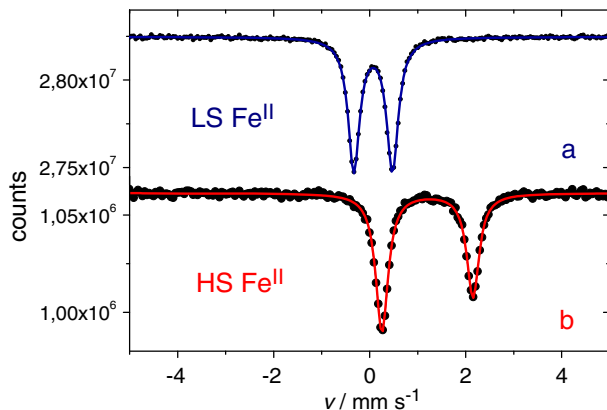
[Fe(glyoxime)₃(BOH)₂] complex $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2] \cdot 6\text{H}_2\text{O}$ (5 mmol), dimethylglyoxime (15 mmol) and H_3BO_3 (15 mmol) were dissolved in 100 ml deoxygenated distilled water, and then borax (75 mmol) was added. The solution was refluxed for 2 h under inert conditions (Ar gas). The precipitated reddish brown crystalline product was filtered, washed with cold water, then dried in vacuo.

[Fe(Me-i-propyl-glyoxH)₂(amine)₂] complexes 2.5 mmol of $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2] \cdot 6\text{H}_2\text{O}$ in 50 ml distilled water and 5 mmol of MePrGlyoxH₂ in 50 ml of 96 % ethanol were mixed. After removal of the air from the solution by bubbling an inert gas (Ar) for 10–15 min, 5 mmol of amine in ethanolic solution was added. The precipitated crystals were filtered, washed with 50 % (v/v) aqueous methanol or ethanol, and dried in air.

The structures of some investigated compounds are shown in Fig. 1.

^{57}Fe Mössbauer spectra of powder samples were recorded in transmission geometry with conventional Mössbauer spectrometers (WISSEL, KFKI) working in constant acceleration mode. The γ -rays were provided by a 3×10^9 Bq $^{57}\text{Co}/\text{Rh}$ source. The measurements were performed at 300 K and at 78 K. Isomer shifts are given

Fig. 2 RT ^{57}Fe Mössbauer spectra of $\text{Fe}(\text{glyoxime})_3(\text{BOH})_2$ (**a**) and $\text{Fe}(\text{Me-i-propyl-glyoxH})_2(2\text{-amino-pyrimidine})_2$ (**b**)



relative to α -iron. The Mössbauer spectra were analyzed by least-square fitting of Lorentzian lines by the help of the MOSSWINN code.

3 Results and discussion

Figure 2 shows ^{57}Fe Mössbauer spectra recorded at room temperature, of selected iron(II)-dioxime complexes, $[\text{Fe}(\text{glyoxime})_3(\text{BOH})_2]$ and $[\text{Fe}(\text{Me-i-propyl-glyoxH})_2(2\text{-amino-pyrimidine})_2]$. The spectrum of $[\text{Fe}(\text{glyoxime})_3(\text{BOH})_2]$ was decomposed well into one doublet.

The Mössbauer parameters are given in Table 1. These are associated with a low-spin Fe^{II} state based on its characteristic Mössbauer parameters [4, 5] in agreement with the expectation for this compound. Furthermore, the doublet reflects solely one single Fe microenvironment being characteristic of $[\text{Fe}(\text{glyoxime})_3(\text{BOH})_2]$ from which it follows that no other Fe microenvironments, consequently, no impurity phases are present in the sample.

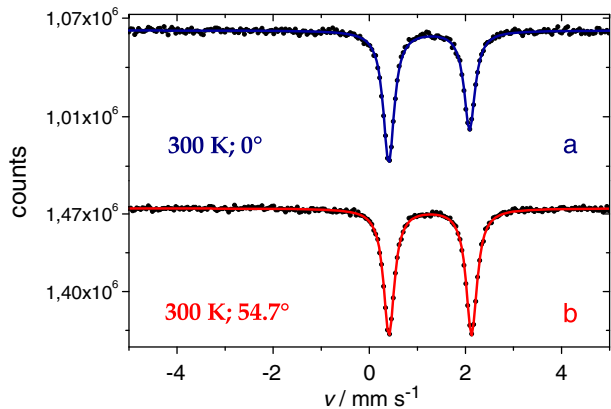
We found the most striking results in connection with dioxime complexes having branched alkyl chains. The spectrum of $[\text{Fe}(\text{Me-i-propyl-glyoxH})_2(2\text{-amino-pyrimidine})_2]$, typical for these compounds, in Fig. 2b is decomposed to an asymmetric doublet with parameters ($\delta = 1.221 \text{ mm}\cdot\text{s}^{-1}$, $\Delta = 1.734 \text{ mm}\cdot\text{s}^{-1}$) which are significantly different from those characteristic of $[\text{Fe}(\text{glyoxime})_3(\text{BOH})_2]$ in Fig. 2a. The parameters of i-propyl-containing derivative (spectrum in Fig. 2b) correspond to a high-spin Fe^{II} state while the spectrum in Fig. 2a shows low-spin $\text{Fe}(\text{II})$ state. In the previous study [1], furthermore, it was found that the spectrum recorded for $[\text{Fe}(\text{Me-Et-glyoxH})_2(2\text{-imidazolidone})_2]$ contains iron in low-spin state, similarly to the spectrum shown in Fig. 2a. The Mössbauer parameters of $[\text{Fe}(\text{Me-Et-glyoxH})_2(2\text{-imidazolidone})_2]$ are also given in Table 1 for comparison. The only difference between $[\text{Fe}(\text{Me-Et-glyoxH})_2(2\text{-imidazolidone})_2]$ and $[\text{Fe}(\text{Me-iPr-glyoxH})_2(2\text{-imidazolidone})_2]$ compounds lies in the side chains of the oximes. Thus we think that the replacement of short alkyl chains to branched ones in iron-bis-glyoximato compounds cause an alteration in the molecular geometry. As a consequence, here the large isopropyl ligand caused shorter iron-nitrogen bond therefore the high-spin state became more favorable.

Table 1 Mössbauer parameters of novel glyoximes at RT

Sample	δ (mm/s)	Δ (mm/s)	w (mm/s)	Spin state
[FeGlyox ₃ (BOH) ₂]	0.072 ± 0.001	0.803 ± 0.002	0.292 ± 0.003	Low
[Fe(Me-Et-glyoxH) ₂ (2-imidazolidone) ₂]	0.228 ± 0.002 ^a	1.420 ± 0.003 ^a	0.276 ± 0.004 ^a	Low ^a
[Fe(Me-i-propyl-glyoxH) ₂ (2-imidazolidone) ₂]	1.245 ± 0.001	1.682 ± 0.002	0.277 ± 0.003	High
[Fe(Me-i-propyl-glyoxH) ₂ (2-amino-pyrimidine) ₂]	1.221 ± 0.001	1.734 ± 0.002	0.295 ± 0.003	High

^aThe data are taken from [2]

Fig. 3 RT ⁵⁷Fe Mössbauer spectra of Fe(Me-i-propyl-glyoxH)₂(2-imidazolidone)₂ taken at normal geometry (**a**) and at magic angle (**b**)



We have observed small but significant differences between the isomer shift values in the two i-propyl-containing compounds (Table 1). The main difference between the structure of these two compounds lies in the axial ligands (Fig. 1., 3rd and 4th structures). Consequently, the difference between the isomer shifts is expected to originate from the different bond character of these ligands in the molecules. The imidazolidone ligand is a stronger electron donor than the amino group therefore it increases the electron density on the 3d orbitals of the iron with a higher value than the amino ligand via the back-coordination. The more 3d electrons lower the density of ‘s’ electrons via the shielding effect therefore it causes a higher isomer shift.

Asymmetry between the intensities of quadrupole split lines in the spectrum of [Fe(Me-i-propyl-glyoxH)₂(2-amino-pyrimidine)₂] of in Fig. 2b was observed. To elucidate the origin of this effect we performed temperature-dependent Mössbauer measurements which excluded the Goldanskii-Karyagin effect [4], and relaxation effects [4] as possible reasons of the asymmetry in line intensities. In order to eliminate the texture effect in the spectrum, then we measured the spectrum of the compound in “magic angle geometry” when the angle between the gamma ray direction and the normal of the sample plane was 54.7° [6]. Figure 3b shows the spectrum taken in magic angle, in comparison with the one recorded in conventional geometry (Fig. 3a). It was found that the line asymmetry completely disappeared from the spectrum when the measurement was performed in magic angle geometry.

Thus we were able to prove that the texture effect is the true reason for the asymmetry of the quadrupole split lines, not the presence of impurity phase(s).

4 Conclusions

^{57}Fe Mössbauer spectroscopy proved to be a convenient tool to check the iron-containing impurities in Fe^{II} dioxime samples obtained in a synthetic way. More importantly, the spin state of iron can be manipulated by replacing the short alkyl chains with branched ones in iron-dioxime complexes. The different electron donor ability of the axial ligands in these complexes can be reflected by the isomer shift.

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